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1,1-Carboboration of Dialkynyltin Compounds using Triorganoboranes of Greatly Different Lewis Acid Strength. 1,4-Stannabora-cyclohexa-2,5-dienes and Characterization of Zwitterionic Intermediates

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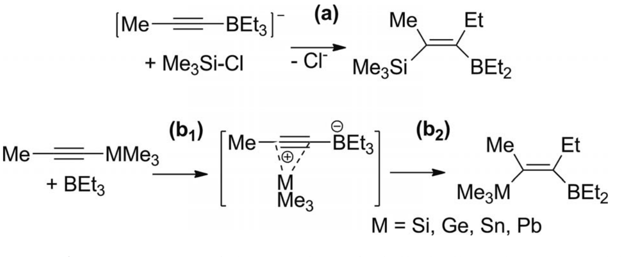
Dedicated to Professor Heinrich Nöth on the Occasion of His 85th Birthday

Keywords: Organotin compounds; Alkynes; 1,1-Carboboration; Side-on-η^2 coordination; Tin; NMR; X-ray spectroscopy

Abstract. Triorganoboranes BR_3, Et-9-BBN, BPh$_3$, and B(C$_6$F$_5$)$_3$, were compared in their reactivity towards various dialkynyl(diorgano)tin compounds ($R^1{}_2$Sn(C≡C–R^2)$_2$ with $R^1{}_2$ = –(CH$_2$)$_5$–, R^2 = H (**a**), R^1 = *n*Bu, R^2 = H (**b**), R^1 = Ph, R^2 = H (**c**), R^1 = R^2 = *n*Bu (**d**)). 1,1-Carboboration took place readily in two consecutive steps (inter- and intramolecular), leading either to stannoles or to 1,4-stannabora-cyclohexa-2,5-dienes, or mixtures thereof. The weakest Lewis-acidic triorganoboranes BEt$_3$ and Et-9-BBN afford selectively stannoles with diethynyltin compounds, whereas the strongly electrophilic B(C$_6$F$_5$)$_3$ leads selectively to 1,4-stannabora-cyclohexa-2,5-dienes for all dialkynyltin compounds studied. In several cases, zwitterionic intermediates could be detected by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, and ^{119}Sn NMR), and the molecular structure of such an intermediate as well as that of the final product, an 1,4-stannabora-cyclohexa-2,5-diene, could be determined by X-ray crystallography.

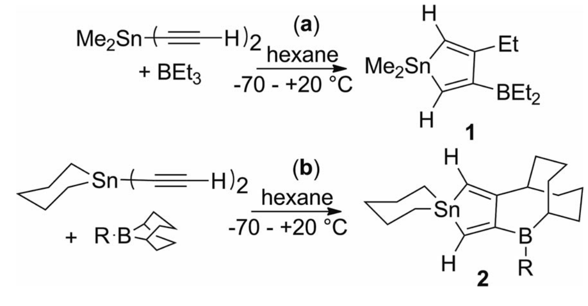
Introduction

Since a great variety of triorganoboranes BR_3 (e.g. R = alkyl, vinyl, aryl, cyclic, non-cyclic) is readily accessible,[1,2] their use in synthesis to form C–C bonds is attractive. In this respect 1,1-carboboration of alkynes has been developed in several ways. Early progress had been made by conversion of BR_3 into trialkyl(alkynyl)borates [R_3B–C≡C–C–R^2]$^-$, followed by their reaction with electrophiles and salt elimination (Scheme 1a).[3] Then, it was found that trialkylboranes react with alkynyltin and some other alkynylmetal derivatives by 1,1-carboboration, almost quantatively and in many cases stereospecifically by migration of the metal fragment along the C≡C bond (Scheme 1b). This reaction turned out to be less prone to side reactions and rather versatile. For instance it allowed to use alkynylmetal compounds with up to four alkynyl groups linked to the metal.[4,5]



Scheme 1. (a) Example of the reaction of trialkyl(alkynyl)borates with an electrophile via salt elimination. (b) Examples of 1,1-ethyloboration of propyn-1-ylmetal compounds (the intermediacy of the zwitterionic species is proposed).

For M = Si the 1,1-ethyloboration requires rather harsh reaction conditions (several hours at 100 °C), indicating that strongly electrophilic triorganoboranes might work better, eventually even with "non-activated" alkynes, as has been convincingly demonstrated by using B(C$_6$F$_5$)$_3$.[6–8] Nevertheless it proved possible to obtain siloles in a most straightforward way from reactions of numerous dialkynylsilanes with the weakly Lewis-acidic trialkylboranes.[9,10] Under much milder conditions, such siloles could also be prepared using B(C$_6$F$_5$)$_3$.[11] The facile and quantitative synthesis of stannoles by the reaction of diethynyltin compounds with various trialkylboranes (Scheme 2) appears to be similarly intriguing. Thus, the stan-



Scheme 2. Examples of 1,1-carboboration reactions of diethynyltin compounds affording stannoles (R = *s*Bu).

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nole **1** was the first example, characterized by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR) in solution,[12] and later on, the molecular structure of **2** was confirmed by X-ray structural analysis.[13]

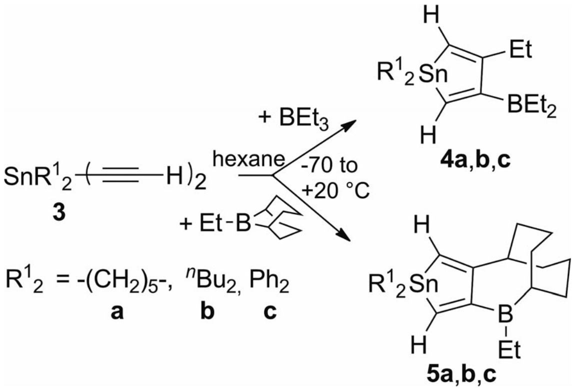
In the presented work we have set out to compare the reactivity of four dialkynyltin compounds **3** ($R^1{}_2$Sn(C≡C–R^2)$_2$ with $R^1{}_2$ = –(CH$_2$)$_5$–, R^2 = H (**a**), R^1 = *n*Bu, R^2 = H (**b**), R^1 = Ph, R^2 = H (**c**), R^1 = R^2 = *n*Bu (**d**)), towards the triorganoboranes BEt$_3$, Et-9-BBN, BPh$_3$, and B(C$_6$F$_5$)$_3$. Particular care was taken to look for zwitterionic intermediates[14–16] in order to reveal mechanistic aspects of the 1,1-carboboration reactions.

Results and Discussion

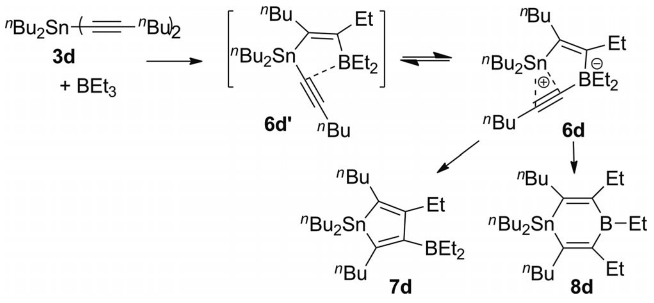
Synthesis and NMR Spectroscopy

The solution-state characterization of organotin compounds by NMR spectroscopy is well documented.[17–19] In the presented work, chemical shifts δ^{119}Sn show the expected pattern due to different substituents. δ^{119}Sn data are particularly helpful for detecting zwitterionic intermediates and to distinguish between different ring sizes. Moreover coupling constants $^{n}J(^{119}\text{Sn},^{13}\text{C})$ or $^{n}J(^{119}\text{Sn},^{1}\text{H})$ give useful information, especially if the tin atom may be found in somewhat extreme bonding situations. Structural elucidation, based as usual on ^{13}C NMR spectroscopy, is further aided by the presence of boron, since ^{13}C(B–C) NMR signals are usually broadened[20] and therefore easy to assign.

Trialkylboranes react with diethynyltin compounds **3a–c** (Scheme 3) via two fast consecutive 1,1-carboborations in the same way as reported previously e.g. for **1**[12] and **2**[13] (Scheme 2), as shown by consistent NMR spectroscopic data sets (Table 1). Therefore, different organyl groups as substituents on tin do not exert a major effect on the course of the 1,1-carboboration reactions. Attempts failed to observe intermediates, and using a large excess, e.g. of BEt$_3$, had no influence.



Scheme 3. Typical 1,1-carboboration reactions of trialkylboranes with diethynyltin compounds.



Scheme 4. 1,1-Ethyloboration of dibutyl(dihexyn-1-yl)tin proceeds via a zwitterionic intermediate **6d**. The activation of the Sn–C≡ bond in **6d′** is indicated by a dashed line.

Substituents R^2 at the C≡C bond other than hydrogen,[21,22] here R^2 = *n*Bu in **3d**, have a significant influence on the product distribution (Scheme 4). Using a 1.1 ratio of starting materials, the formation of the fairly long-lived zwitterionic intermediate **6d** can be readily detected, most likely a result of kinetic stabilization due to the *n*Bu groups at both tin and C≡C bonds. NMR signals of **6d′**, the precursor of **6d** (Scheme 4)

Table 1. Selected NMR parameters for stannoles **1** (for comparison), **4**, **5**, and **7d** $^{a)}$.

	δ^{13}C C2	C3	C4	C5	R/BR_2	δ^{119}Sn	δ^{11}B
1 $^{b)}$	127.8 [410.4]	175.3 br	162.7 [89.9]	121.0 [484.4]	30.9 [62.6], 13.2/21.4 br, 9.2	19.5	85.0
4a $^{c)}$	126.6 [382.7]	175.0 br	162.4 [84.4]	119.5 [456.0]	30.9 [61.9], 13.0/21.2 br, 9.0	–21.7	86.7
4b $^{d)}$	128.1 [364.9]	175.8 br	163.3 [79.1]	121.3 [433.9]	31.0 [59.0], 13.2/21.3 br, 9.2	22.9 (25.0)	83.2
4c $^{e)}$	124.8 [441.1]	176.5 br	164.7 [99.6]	118.4 [517.7]	30.5 [67.6], 12.7/21.1 br, 8.9	–46.9 (23.4)	84.5
5a $^{f]}$	138.6 [373.8]	171.3 br	170.6 [71.1]	120.8 [436.6]	23.7 br, 11.3/33.5 br, 31.4, 22.2, 33.6, 43.2 [64.0]	–37.8 (29.1)	79.9 (1230)
5b $^{g)]}$	139.4 [360.5]	171.9 br	170.0 [66.4]	122.3 [418.3]	23.7 br, 11.3/33.7 br, 31.6, 22.2, 33.7, 43.4 [60.5]	8.1 (18.0)	80.1 (1460)
5c $^{h]}$	136.0 [435.0]	176.1 br	172.7 [83.9]	119.8 [503.1]	23.9(br), 11.4/33.9 br, 31.5, 22.2, 33.8, 43.2 [70.8]	–59.2 (22.1)	80.9 (1410)
7d $^{i)}$	142.4 [380.8.6]	165.8 br [44.2]	152.4 [104.7]	141.6 [428.6]	27.0 [60.6], 12.5/21.2 br, 9.1	0.4 (17.2)	90.4 (2570)

a) In C$_6$D$_6$ at 296 K; br. denotes the broad ^{13}C NMR signal of carbon linked to boron; coupling constants $^{n}J(^{119}\text{Sn},^{13}\text{C})$ are given in brackets. b) Ref. [12]; in CD$_2$Cl$_2$ at 299 K, other ^{13}C NMR spectroscopic data: –9.3 [329.7] (Sn–CH$_3$). c) Ref. [13]; other ^{13}C NMR spectroscopic data: 11.3 [311.5] (Sn–CH$_2$), 28.5 [32.3] (CH$_2$), 32.4 [53.9] (CH$_2$). d) In [D$_8$]tol; other ^{13}C NMR spectroscopic data: 11.9 [337.0] (Sn–CH$_2$), 29.9 [22.4] (CH$_2$), 27.3 [50.8] (CH$_2$), 13.8 (CH$_3$). e) Other ^{13}C NMR spectroscopic data: 138.5 [506.5] (C-*i*), 137.1 [40.0] (C-*o*), 128.6 [51.8] (C-*m*), 129.0 [11.4] (C-*p*). f) In CDCl$_3$, other ^{13}C NMR spectroscopic data: 11.1 [313.7] (Sn–CH$_2$), 28.4 [31.7] (CH$_2$), 31.7 [53.1] (CH$_2$). g) In CDCl$_3$, other ^{13}C NMR spectroscopic data: 11.7 [340.7] (Sn–CH$_2$), 29.6 [22.6] (CH$_2$), 27.0 [50.6] (CH$_2$), 13.7 (CH$_3$). h) In CDCl$_3$, other ^{13}C NMR spectroscopic data: 138.4 [509.9] (C-*i*), 137.1 [39.8] (C-*o*), 128.6 [51.2] (C-*m*), 129.0 [10.0] (C-*p*). i) No assignent of ^{13}C(Sn-*n*Bu) resonances because of overlap with signals for **8d**.

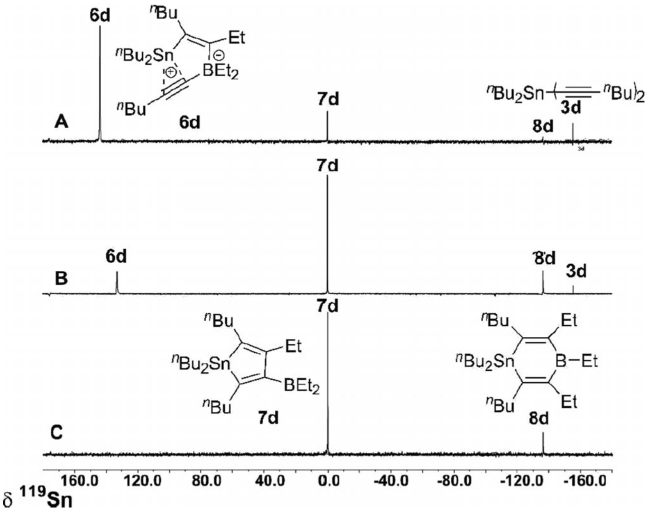


Figure 1. 149.1 MHz $^{119}Sn\{^{1}H\}$ NMR spectra of the reaction mixture of **3d** with BEt_3 (in C_6D_6 at 296 K). (A) 1 h after the mixture has reached room temp.; (B) after 5 h at room temp.; (C) after 17 h at room temp. The ^{119}Sn NMR signal of **8d** is almost two-times broader than that of **7d**, as a result of unresolved scalar three-bond ^{119}Sn-^{11}B spin-spin coupling (two equivalent coupling pathways in **8d**).

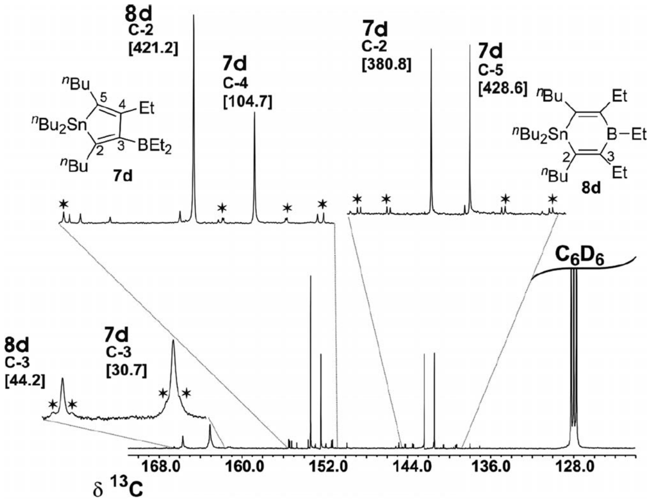


Figure 2. 100.5 MHz $^{13}C\{^{1}H\}$ NMR spectrum (in C_6D_6, at 296 K; shown is the region of olefinic carbon atoms) of the final mixture containing **7d** and **8d** $^{117/119}Sn$ satellites are marked by asterisks, and coupling constants $^{n}J(^{119}Sn,^{13}C)$ in Hz are given in brackets. Note the broadened ^{13}C NMR signals for ^{13}C nuclei linked directly to boron owing to partially relaxed ^{13}C-^{11}B spin-spin coupling.[20]

were not observed. Interestingly, the selectivity of the final intramolecular 1,1-carboboration is lost, The stannole **7d** and the 1,4-stannabora-cyclohexa-2,5-diene **8d** are formed in a ratio of about 60:40 by intramolecular 1,1-vinylo- and 1,1-ethyloboration, respectively.

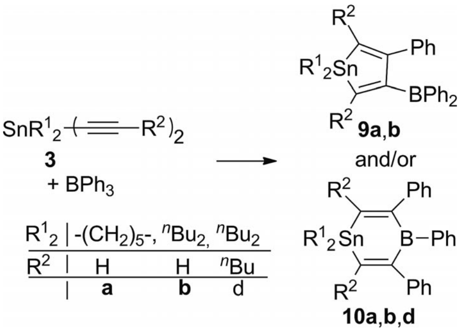
The reaction shown in Scheme 4 can be conveniently monitored by ^{119}Sn NMR spectroscopy (Figure 1). The ^{119}Sn nucleus in **6d** is typically deshielded[14–16] when compared with chemical shifts $\delta^{119}Sn$ of tetraorganotin compounds.[17] This is attributed to the partial positive charge on tin in the cationic fragment, which is stabilized by side-on (η^2) coordination to the remaining C≡C bond. The ^{119}Sn NMR signal of **6d** appears to be sensitive to small changes in temperature and concentration of other species present in solution (compare Figure 1, A and B). All NMR spectroscopic data of **7d** (Table 1) and **8d** (Table 2) are in support of the proposed structures (see Figure 2 for ^{13}C NMR spectroscopy of the final mixture of products).

In order to increase the Lewis-acid strength with respect to trialkylboranes, triphenylborane BPh_3 was used (Scheme 5). Monoalkynyltin compounds react readily with BPh_3 to give clean 1,1-carboboration products.[23] Similarly, the reactions of BPh_3 with dialkynyltin compounds proceed fast, even at low temperature. However, the formation of final major products was accompanied by many side products in minor quantities, most of which appeared to be phenyltin compounds (suggested

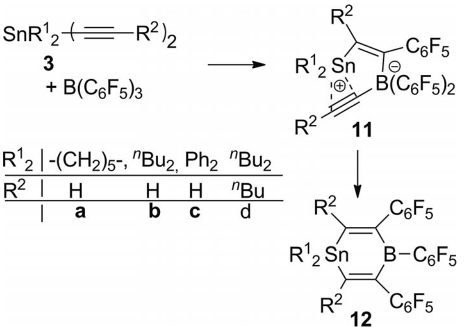
Table 2. Selected NMR parameters of 1,4-stannabora-cyclohexa-2,5-dienes **8d**, **10d**, and **12** a).

	$\delta = {}^{13}C$ =C(2)–Sn	B–C(3)=	3-R	B*R*	*R*$^1_2$Sn	$\delta = {}^{119}Sn$	$\delta = {}^{11}B$
8d b)	153.4 [421.2]	163.1 [30.7]				–134.8 (42.0)	72.9 (1500)
10d c)	164.7 [390.1]	161.0 [36.1]	143.6 [63.6], 128.9, 127.6, 126.1	145.6 br, 131.8, 126.1, 125.1	12.0 [336.6]	–133.8 (24.1)	60.4 (2110)
12a d)	179.2 [341.8]	150.0 br	121.2 t ‖19.4‖ (*i*)	115.9 br (*i*)	11.7 [356.8] 27.8 [34.1], 30.7 [69.4]	–176.5 (35.0)	55.5 (2500)
12b e)	180.0 [319.7]	149.7 [50.8] br	121.4 t ‖20.5‖ [51.7] (*i*)	116.4 br (*i*)	12.3 [386.6], 29.3 [27.1] 27.0 [60.6] 13.6	–134.4 (25.0)	57.0 (2100)
12c f)	174.6 [409.5]	150.6 br	121.4 t ‖ 19.9‖ (*i*)	116.4 br (*i*)	134.4 (*i*), 137.1 [41.7] (*o*), 129.8 [59.1] (*m*), 130.6 [12.8] (*p*)	–212.8 (18.5)	58.0 (3300)
12d g)	197.8 [336.2]	150.0 br	118.4 t ‖22.3‖ (*i*)	br (not observed)	13.7 [357.4] 29.2 [25.1] 27.3 [60.6] 13.6	–129.7 (16.2)	56.8 (2070)

a) In C_6D_6 at 296 K; line widths $h_{1/2}$ are given in parentheses, coupling constants $^{n}J(^{119}Sn,^{13}C)$ in Hz in brackets; coupling constants $^{n}J(^{19}F,^{13}C)$ and $^{n}J(^{19}F,^{19}F)$ in Hz in ‖ &par. b) Other ^{13}C NMR spectroscopic data not assigned owing to overlapping signals. c) In $CDCl_3$, other ^{13}C NMR spectroscopic data: 12.0 [336.3] (CH_2), 13.6 (CH_3), 14.0 (CH_3), 22.8, 27.4 [61.7], 29.5 [21.0], 33.2 [11.2], 36.5 [44.8]. d) ^{19}F NMR spectroscopic data: C_6F_5 group: –143.1 m (*o*), –156.5 t ‖20.5‖ (*p*), –162.7 m ‖7.2‖ ‖20.5‖ (*m*), B–C_6F_5 group: –132.3 m (*o*), –150.7 t ‖20.5‖ (*p*), –161.4 m ‖7.7‖ ‖ 20.5‖ (*m*). e) ^{19}F NMR spectroscopic data: C_6F_5 group: 143.4 m (*o*), –156.6 t ‖21.5‖ (*p*), –162.7 m ‖8.4‖ ‖ 21.5‖ (*m*), B–C_6F_5 group: –132.5 m (*o*), –150.7 t ‖20.5‖ (*p*), –161.3 m ‖8.2‖ ‖20.5‖ (*m*). f) ^{19}F NMR spectroscopic data: C_6F_5 group: –143.0 m (*o*), –156.6 t ‖21.3‖ (*p*), –162.9 m ‖8.5‖ ‖21.3‖ (*m*), B-C_6F_5-group: –132.3 m (*o*) –150.7 t ‖22.6‖ (*p*), –161.4 m ‖8.3‖ ‖22.6‖ (*m*). g) ^{19}F NMR spectroscopic data: C_6F_5 group: –140.5 m (*o*), –156.1 t ‖21.1‖, (*p*), –162.9 m (*m*), B–C_6F_5 group: –132.7 m (*o*), –153.1 t ‖21.1‖ (*p*), –162.1 m (*m*).



Scheme 5. 1,1-Phenyloboration of dialkynyltin compounds.



Scheme 6. 1,1-Carboboration of dialkynyltin compounds **3a**–**d** using $B(C_6F_5)_3$.

by ^{119}Sn NMR spectra), most likely as the result of alkynyl/phenyl exchange. These side reactions hampered the search for zwitterionic intermediates. Nevertheless, mixtures of stannoles [in minor quantity, $\delta^{119}Sn$ –23.3 ppm (**9a**), 24.1 ppm (**9b**)], and 1,4-stannabora-cyclohexa-2,5-diene derivatives [$\delta^{119}Sn$ –152.0 ppm (**10a**), –113.6 ppm (**10b**)] were clearly identified by characteristic NMR signals, and in the case of **3d**, the 1,4-stannabora-cyclohexa-2,5-diene **10d** (Table 2) was the preferred product (>85 %). Apparently, increasing Lewis-acid strength of the borane directs the course of the reaction towards the six-membered ring, and this tendency is further augmented by substituents R^2 other than hydrogen.

The results for BPh_3 prompted the study of $B(C_6F_5)_3$ as a strong Lewis acid for 1,1-carboboration reactions of alkynyltin compounds. However, first experiments with monoalkynyltin compounds $Me_3Sn–C{\equiv}C–R^2$ (R^2 = H, Me) did not give clean products, except of $Me_3Sn–C_6F_5$, [$\delta^{119}Sn$ –12.4 ppm, ttd, $^3J(^{119}Sn,^{19}F)$ = 23.0, $^4J(^{119}Sn,^{19}F)$ = 8.1, $^5J(^{119}Sn,^{19}F)$ = 8.1 Hz] and only traces (R^2 = H) or small amounts (R^2 = Me) of 1,1-carboboration products analogous to those in Scheme 1b. Measuring NMR spectra of reaction solutions in hexane revealed intense ^{119}Sn NMR signals with $\delta^{119}Sn$ around 260 ppm, typical of the stabilized cation Me_3Sn^{+}[24] and ^{11}B NMR signals with $\delta^{11}B$ = –1 ppm, typical of tetracoordinate boron,[25] pointing towards ionic intermediates. So far, these compounds could not be isolated or identified.

Turning to the 1,1-carboboration of dialkynyltin compounds **3** with $B(C_6F_5)_3$, much better results and clean products were obtained (Scheme 6). In all cases studied, the zwitterionic intermediates **11** could be readily identified by NMR spectroscopy (Table 3, Figure 3, and Figure 4) in solution or even isolated (**11a**) and studied by X-ray crystallography (vide infra).

Whereas the zwitterionic intermediate **6d** rearranged to a mixture of the final products **7d** and **8d** (Scheme 4), the analogous intermediates **11** afforded selectively the 1,4-stannabora-cyclohexa-2,5-diene derivatives **12**. This is clearly evident from all NMR spectroscopic data for solutions of **12** (Table 2, Figure 5) and in the case of **12a**, crystalline materials for X-ray structural analysis could be isolated (vide infra).

Table 3. Selected NMR Parameters of zwitterionic intermediates **11** a).

δ^1H			$\delta^{13}C$	$\delta^{19}F$		$\delta^{11}B$ ($h_{1/2}$)	$\delta^{119}Sn$ ($h_{1/2}$)
	=C–H	≡C–H	$R^1{}_2Sn$	C_6F_5	$B(C_6F_5)_2$		
11a	6.28 br [244.3]	2.57 [7.1]	21.9 [276.6] ($Sn-CH_2$), 26.9 [38.1] (CH_2), 29.6 [72.8] (CH_2)	–141.4 m (*o*), –157.0 t $\|21.7\|$ (*p*), –163.8 dt $\|7.7\|$ $\|21.7\|$ (*m*)	–130.8 m (*o*) –158.0 t $\|20.7\|$ (*p*), –164.9 dt $\|8.7\|$ $\|20.7\|$ (*m*)	–15.4 (126.0)	225.8 (125.0)
11b b)	6.30 br [220.1]	2.12 [9.9]	21.8 [306.1] ($Sn-CH_2$), 27.7 [20.6] ($Sn-CH_2–CH_2$), 26.8 [68.8] (CH_2), 13.4 (CH_3)	–141.1 m (*o*), –157.3 t $\|21.9\|$ (*p*), –163.8 dt $\|7.2\|$ $\|21.9\|$ (m)	–130.8 m (*o*), –158.3 t $\|21.2\|$ (*p*), –164.9 dt $\|8.1\|$ $\|21.2\|$ (*m*)	–15.3 (116.0)	241.5 (120.0)
11c c)	6.26 br [242.4]	2.34 [11.5]	134.4 [n.b.] (C-*i*), 137.1 [41.7] (C-*o*), 129.8 [59.1] (C-*m*), 130.6 [12.8] (C-*p*)	–140.5 m (*o*), –157.1 t $\|21.5\|$ (*p*), –164.0 dt $\|7.5\|$ $\|21.5\|$ (*m*)	–130.5 m (o) –158.3 t $\|21.2\|$ (*p*) –165.1 dt $\|8.3\|$ $\|20.9\|$ (*m*)	–15.2 (203.0)	68.9 (110.0)
11d d)	–	–	21.1 [279.7] ($Sn-CH_2$), 28.0 [21.7] ($Sn-CH_2–CH_2$), 27.0 [67.0] (CH_2), 13.4 (CH_3)	–140.2 m (*o*), –157.8 t $\|21.3\|$ (*p*), –164.1 m (*m*)	–130.3 m (*o*), –159.6 t $\|20.7\|$ (*p*), –165.6 dt $\|8.3\|$ $\|20.7\|$ (*m*)	–12.4 (141.0)	240.3 (44.3)

a) In C_6D_6 at 296 K, line widths $h_{1/2}$ in Hz in parentheses, coupling constants $^nJ(^{119}Sn,X)$ (X = $^{19}F,^{13}C,^1H$) in Hz in brackets, coupling constants $^nJ(^{19}F,^{13}C)$ and $^nJ(^{19}F,^{19}F)$ in Hz in $\|$ $\|$; (br) denotes broad ^{13}C NMR signals for carbon atoms linked to boron. b) Other ^{13}C NMR spectroscopic data: 100.8 (br., B–C≡), 118.4 [48.9] (≡C–Bu), 122.2 [55.8] (≡C–H), 153.8 [603.6] (Sn–CH=). c) Other ^{13}C NMR spectroscopic data: 122.2 [55.8] (≡C–H), 153.8 [603.6] (Sn–CH=);. d) Other ^{13}C NMR spectroscopic data: 12.9 (CH_3), 13.7 (CH_3), 20.6 (CH_2), 21.4 (CH_2), 22.5 [6.3] (CH_2), 30.0 (CH_2), 34.8 [32.7] (CH_2), 36.1 [96.4] (CH_2),100.8 (br., B–C≡), 118.4 [48.9] (≡C–Bu), 119.0 (t, $\|21.5\|$], (*i*), C_6F_5), 120.6 (br., (*i*), $B–C_6F_5$), 155.3 [490.5] (Sn–C=), 154.9 (br., =C–B).

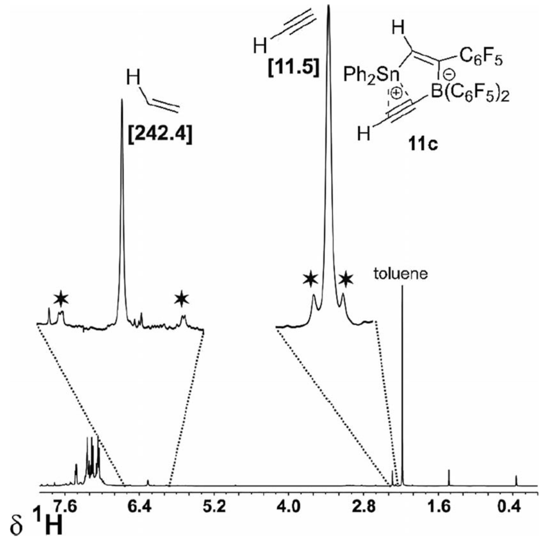


Figure 3. 399.8 MHz ^{1}H NMR spectrum of the zwitterionic intermediate **11c** (in C_6D_6 at 296 K). $^{117/119}$Sn satellites are marked by asterisks and coupling constants $^{n}J(^{119}Sn,^{1}H)$ in Hz are given in brackets.

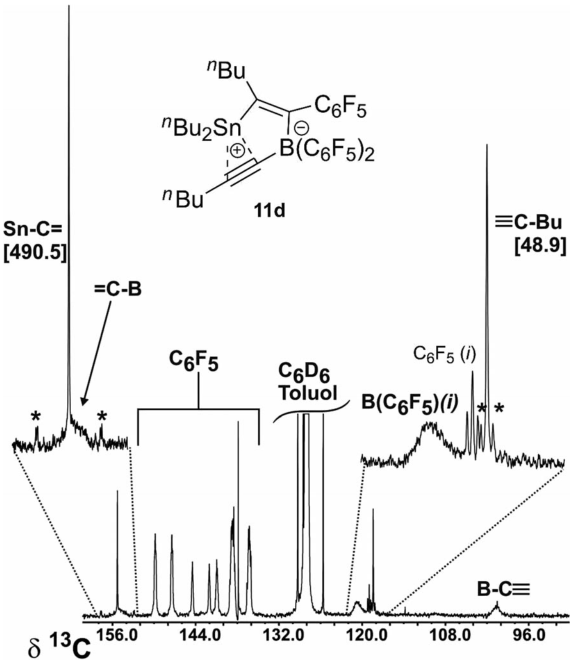


Figure 4. 100.53 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the intermediate **11d** (the region for unsaturated carbon atoms is shown; in C_6D_6 at 296 K). $^{117/119}$Sn satellites are marked by asterisks and coupling constants $^{n}J(^{119}Sn,^{13}C)$ in Hz are given in brackets. Note the broadened ^{13}C NMR signals for ^{13}C nuclei linked diretly to boron owingt to paartially relaxed ^{13}C-^{11}B spin-spin coupling.[20]

X-ray Structural Analyses of the Zwitterionic Intermediate 11a and the 1,4-Stannabora-cyclohexa-2,5-diene Derivative 12a

The molecular structures of **11a** and **12a** are shown in the Figure 6 and Figure 8, respectively. Intermolecular interactions appear to be negligible. In contrast with transition metals, there are only few examples known, where an alkynyl group is coordinated side-on (η^2) to a group-14 metal.[14–16] To the best of our knowledge, **11a** is the first example with side-on coordina-

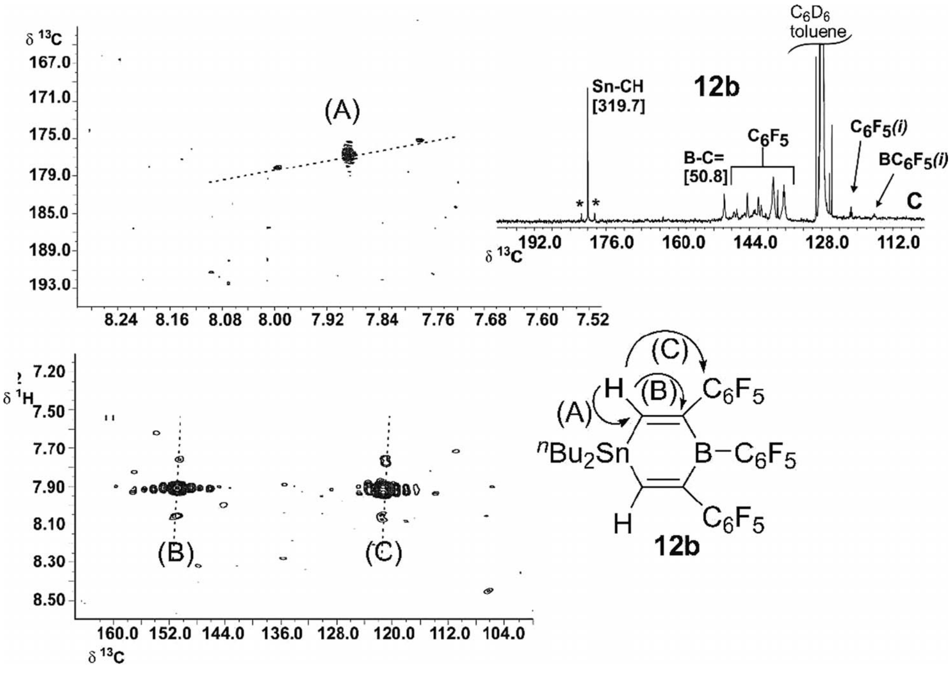


Figure 5. 100.5 MHz $^{13}C\{^{1}H\}$ NMR spectrum (right) of the 1,4-stannabora-cyclohexa-2,5-diene derivative **12b** (in C_6D_6 at 296 K; shown is the region for olefinic and aromatic carbon atoms). $^{117/119}$Sn-satellites are marked by asterisks, and coupling constants $^{n}J(^{119}Sn,^{13}C)$ in Hz are given in brackets. The results of two-dimensional (2D) ^{1}H-^{13}C correlations (HSQC[26]) based on $^{1}J(^{13}C,^{1}H)$ (A), $^{2}J(^{13}C,^{1}H)$ (B), and $^{3}J(^{13}C,^{1}H)$ (C) are shown on the left side. The $^{117/119}$Sn satellites of the cross peaks are connected by dotted lines to indicate the positive tilt in all three cases. This proves[27] that the signs of $^{2}J(^{119}Sn,^{1}H)$ and of $^{n}J(^{119}Sn,^{13}C)$ are alike for $n = 1$ (A), 2 (B), 3 (C). Since for vinyl tin compounds the sign of $^{2}J(^{119}Sn,^{1}H) < 0$ is known,[28] the signs of $^{n}J(^{119}Sn,^{13}C)$ were determined here as < 0.

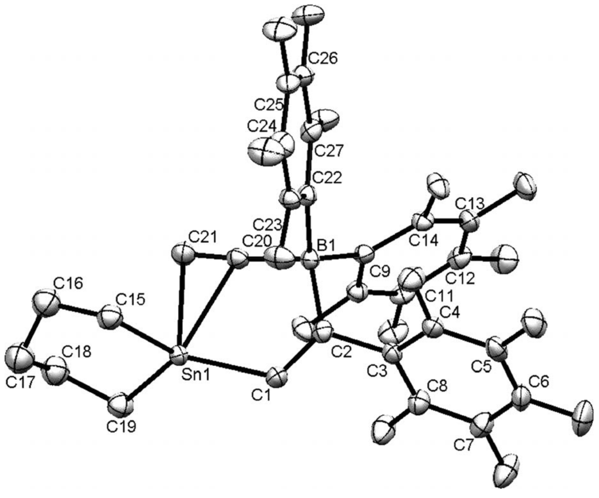
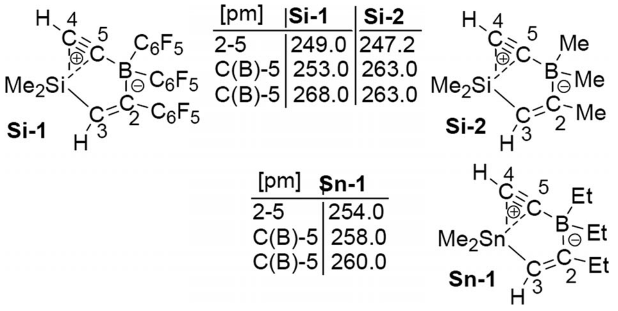


Figure 6. Molecular structure of the zwitterionic intermediate **11a** (ORTEP, 50 % probability, hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths /pm and angles /°: Sn1–C1 211.0(4), Sn1–C20 252.0(3), Sn1–C21 252.7(4), Sn1–C15 212.2(4), Sn1–C19 213.0(4), B1–C2 163.7(5), B1–C20 161.9(5), B1–C9 164.2(5), B1–C22 164.9(6), C1–C2 133.1(5), C20–C21 120.3(6), C2–C3 150.8(5), C1–Sn1–C20 78.04(14), C1–Sn1–C21 105.06(4), C20–Sn1–C21 27.59(13), C1–Sn1–C15 124.80(16), C1–Sn1–C19 125.65(17), C15–Sn1–C19 103.90(17), Sn1–C1–C2 120.02(3), B1–C2–C1 124.4(3), C1–C2–C3 116.4(3), B1–C20–C21 175.6(4), C2–B1–C20 108.1(3), Sn1–C20–B1 106.2(2), C21–Sn1–C15 95.52(15), C20–Sn1–C19 111.91(15), C21–Sn1–C19 91.33(15), C20–Sn1–C15 106.84(15).



[pm]	Si-1	Si-2
2-5	249.0	247.2
C(B)-5	253.0	263.0
C(B)-5	268.0	263.0

[pm]	Sn-1
2-5	254.0
C(B)-5	258.0
C(B)-5	260.0

Figure 7. Some calculated non-bonding C–C distances for optimized geometries of zwitterionic intermediates [**Si-1**, **Si-2**: B3LYP/6-311+G(d,p); **Sn-1**: B3LYP/LanL2DZ].

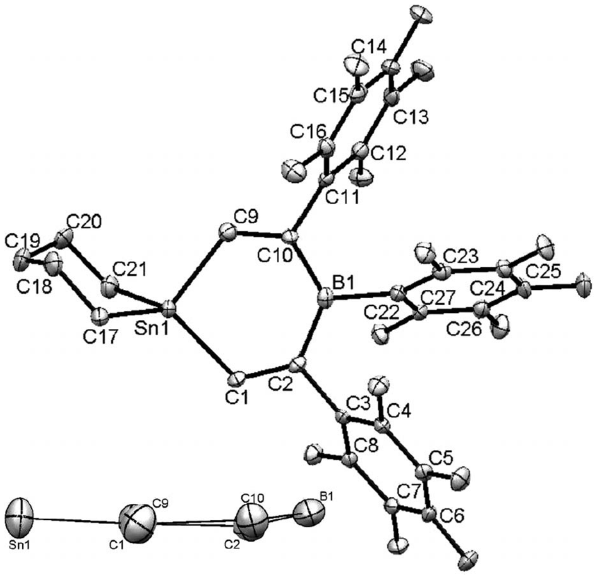


Figure 8. Molecular structure of **12a** (ORTEP, 40 % probability; hydrogen atoms are omitted for clarity), and a side view of the 1,4-stannabora-cyclohexa-2,5-diene. Selected bond lengths /pm and angles /°: Sn1–C1 213.3(4), Sn1–C9 213.0(5), Sn1–C21 213.6(4), Sn1–C17 214.6(4), C1–C2 135.2(6), C2–B1 156.2(7), C9–C10 135.4(6), C10–B1 155.2(7), B1–C22 160.8(6), C2–C3 149.9(6), C10–C11 149.6(6), C1–Sn1–C9 98.16(17), C9–Sn1–C21 107.89(19), C9–Sn1–C17 112.11(17), C1–Sn1–C17 117.84(18), C1–Sn1–C21 122.33(18), Sn1–C1–C2 120.4(4), Sn1–C9–C10 122.8(4), B1–C2–C1 126.5(4), B1–C10–C9 124.9(4), C2–B1–C10 127.0(4), C2–B1–C22 115.6(4), C10–B1–C22 117.3(4), C3–C2–B1 116.5 (4), C11–C10–B1 118.9(4), C3–C2–C1 117.0(4), C11–C10–C9 117.0(4).

tion of an ethynyl group to tin. Similarly, **12a** appears to be the first example of a structurally characterized 1,4-stannabora-cyclohexa-2,5-diene.

The surroundings of the tin atom in **11a** are pyramidal, although not far from trigonal planar (sum of bond angles at tin: 354.4°), as one would expect for a "free" triorgantin cation. The bond lengths Sn–C1, Sn–C15, Sn–C19 (about 211 pm) are slightly shorter than Sn–C bonds in tetraorganotin compounds (see, for example **12a**), whereas for the side-on coordination the bond lengths Sn–C20 (252.0 pm) and Sn–C21 (252.7 pm) are elongated and almost identical. In comparable situations marked differences have been observed.[14–16] Both the C1=C2 and the C20≡C21 bond lengths are in the expected range, apparently unaffected by the neighborhood to positively charged tin, the negatively charged borate unit, and side-on coordination. The surroundings of the boron atom in **11a** correspond to a slightly distorted tetrahedron, and the B–C distances are in the usual range for tetra-coordinate boron.

Since **11a** rearranges finally into **12a** by transfer of one of the C_6F_5 groups (C9, C22) from boron to the neighboring positively charged alkynyl carbon atom C20, the comparison between the non-bonding distances C2–C20 (263.4 pm), C22–C20 (252.8 pm), and C9–C20 (265.9 pm) is meaningful. The shorter distance for C22–C20 when compared with C2–C20 may be one reason for preferred transfer of the C_6F_5 group. The experimental geometry and all bond lengths for **11a** are reasonably well reproduced by calculations (B3LYP/LANL2DZ [29]) including the intramolecular non-bonding distances. Calculations for the non-detected intermediate **Sn-1** (Figure 7; presumably the precursor of stannole **1**) show a different pattern for the distances between carbon atoms in the surroundings of the boron atom, fitting to the formation of stannole **1**. Similar calculations carried out on a higher level of theory [B3LYP/6-311+G(d,p)[30,31]] for the intermediates **Si-1** and **Si-2** reveal a situation comparable with that in **Sn-1** (Figure 7), in particular for the aforementioned non-bonding distances, This is in agreement with the preferred formation of siloles via 1,1-carboboration of dialkynylsilanes, independent of the nature of the triorganoborane.

The surroundings of the tin atom in **12a** correspond to a distorted tetrahedron, and those of the boron atom are trigonal planar, within the experimental error (Figure 8). The arrangement of the 1,4-stannabora-cyclohexa-2,5-diene deviates from planarity, with the tin and the boron atom shifted slightly into the same direction (Sn: 7.5 pm, B: 11.7 pm) out of the best plane formed by the olefinic carbon atoms C1,C2,C9,C10. The bond lengths Sn–C between 213.0 pm and 214.6 pm are in the typical range for tetraorganotin compounds. The endocyclic bond lengths B–C (B–C2 156.2 pm, B–C10 155.2 pm) are markedly shorter than the exocyclic one (B–C22 160.8 pm), all being shorter than in **11a**.

Conclusions

The strongly electrophilic triorganoborane $B(C_6F_5)_3$ exerts a remarkable influence on the final products of 1,1-carboboration of dialkynyltin compounds, when compared with silanes.[10,11] In contrast with weakly Lewis-acidic triethylborane BEt_3 or Et-9-BBN, the reactions of $B(C_6F_5)_3$ with all dialkynyltin compounds studied herein afford selectively 1,4-stannabora-cyclohexa-2,5-dienes. The proposed mechanism of 1,1-carboboration reactions[14–16] is further supported by identification and structural characterization of zwitterionic intermediates, and the molecular structure of a 1,4-stannabora-cyclohexa-2,5-diene could be established for the first time.

Experimental Section

General and Starting Materials: All preparative work as well as handling of the samples was carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Diphenyltin dichloride, dimethyltin dichloride, dibutyltin dichloride, triethylborane, and ethynylmagnesium bromide in THF were commercially available and used as received. Diethynyl(dimethyl)stannane was prepared as described,[32] and the synthesis of **3a**, **3b**, and **3d** was carried out in the same way, using the commercially available diorganotin dichlorides or $(CH_2)_5SnBr_2$.[33] **3d** was prepared from *n*$BuSnCl_2$ and two equivalents of LiC≡C-*n*Bu.[34] NMR measurements in $CDCl_3$, C_6D_6, and [D_3]Tol (concentration ca. 5–10 %) with samples in 5 mm tubes at 23 ± 1 °C: Varian Inova 400 MHz spectrometer for ^1H, ^{11}B, ^{13}C, and ^{119}Sn NMR; chemical shifts are given relative to Me_4Si [δ^1H ($CHCl_3$) = 7.24; $\delta^{13}C$ ($CDCl_3$) = 77.0; δ^1H (C_6HD_5) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0; δ^1H ($C_6D_5CHD_2$) = 2.03; $\delta^{13}C$ ($C_6D_5CD_3$) = 20.4; external Me_4Sn [$\delta^{119}Sn$ = 0 for $\Xi(^{119}Sn)$ = 37.2906 MHz]; external $CFCl_3$ [$\delta^{19}F$ = 0 for $\Xi(^{19}F)$ = 94.0940 MHz; external BF_3–OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.0840 MHz]. Chemical shifts are given to ±0.1 ppm for ^{13}C and ^{119}Sn, and ±0.4 ppm for ^{11}B; coupling constants are given ±0.4 Hz for $J(^{119}Sn,^{13}C)$. ^{119}Sn NMR spectra were measured directly by single pulse methods or by using the refocused INEPT pulse sequence,[35] based on $^2J(^{119}Sn,^1H)$ (50 –100 Hz) after optimizing the delay times in the pulse sequence. Melting points (uncorrected) were determined with a Büchi 510 melting point apparatus. All quantum chemical calculations were carried out using the Gaussian 09 program package.[36]

1,1-Carboboration of Diethynyltin Compounds using Trialkylboranes (BEt_3, Et-9-BBN): The synthesis of **1**[12] and **2**[13] were reproduced, and similar conditions were used for the reactions of **3a**–**c**. A solution of the diethynyltin compound (1.1 mmol) in hexane (20 mL) was cooled to –78 °C. After adding the equimolar amount of the respective trialkylborane through a syringe, the stirred colorless mixture was warmed to room temp., by which a yellow color developed. After 30 min at room temp., all volatile materials were removed in a vacuum. NMR spectra of the yellow to brown oily products showed the quantitative formation of the stannoles **4** and **5** [> 97 % pure (NMR)]. Further attempts at purification by chromatography on silica or various types of Al_2O_3 led to decomposition, as was found previously for similar stannoles.

4a: $\delta\,^1H$ ([D_8]toluene, [$J(^{119}Sn,^1H)$]) = 0.86, 1.18 (t, 6 H, 4 H, q, BEt_2), 0.94, 2.14 (t, 3 H, 2 H, m, 4-Et), 1.09 [52.6] (m, 4 H, $SnCH_2$), 1.74 [82.3] (m, 4 H, CH_2), 1.31 (m, 2 H, CH_2),, 6.04 [164.7] (s, 1 H, H-2), 6.02 [162.6] (s, 1 H, H-5). **4b**: $\delta\,^1H$ ([D_8]toluene, [$J(^{119}Sn,^1H)$]) = 0.81 (t, 6 H, CH_3), 0.89 (4 H, CH_2), 0.96 (6 H,), 1.03 (m, 7 H), 1.26 (m, 8 H), 2.23 (2 H, q), 6.07 [151.0] (s, 1 H, H-2), 6.13 [154.2] (s, 1 H, H-5). **4c**: $\delta\,^1H$ ($CDCl_3$, [$J(^{119}Sn,^1H)$]) = 1.26, 0.88 (q, 10 H, t, BEt_2), 2.21, 1.01 (q, 5 H, t, 4-Et), 6.04 [163.5] (s, 1 H, H-5), 6.11 [162.2] (s, 1 H, H-2), 7.15–7.27 (m, 6 H, $SnPh_2$), 7.42–7.50 (m, 4 H, $SnPh_2$).

5a: $\delta\,^1H$ ($CDCl_3$, [$J(^{119}Sn,^1H)$]) = No assignment in the range of alkyl groups because of severe overlap; 6.13 [161.5] (s, 1 H, H-2), 6.43 [162.1] (s, 1 H, H-5). **5b**: $\delta\,^1H$ ($CDCl_3$, [$J(^{119}Sn,^1H)$]) = 0.91 (t, 6 H, CH_3), 1.07 (3 H, 3 H, CH_3 1.20 (t, 4 H, CH_2, 7.6 Hz), 1.29–1.48 (m, 8 H, CH_2), 1.50–1.73 (m, CH, CH_2, BBN), 1.92–2.11 (m, CH_2, BBN), 3.22 (1 H, qt, CH, BBN), 5.93 [154.0] (s, 1 H, H-5), 6.78 [153.5] (s, 1 H, H-2). **5c**: $\delta\,^1H$ ($CDCl_3$, [$J(^{119}Sn,^1H)$]) = 0.89, 1.24 (t, 3 H, 2 H, q, BEt), 1.36–1.51 (m, CH, CH_2, BBN), 1.76–1.91 (m, CH_2, BBN), 3.10 (1 H, qt, CH, BBN), 5.86 [164.4] (s, 1 H, H-5), 6.65 [163.3] (s, 1 H, H-2), 7.17–7.25 (m, 6 H, $SnPh_2$), 7.33–7.59 (m, 4 H, $SnPh_2$).

1,1-Ethyloboration of Dibutyl-bis(hexyn-1-yl)tin (1:1 Reaction): Triethylborane (58.4 mg, 86 µL, 0.5954 mmol) was added through a syringe to a cooled (–78 °C) solution of **3d** (235.5 mg, 0.5954 mmol) in hexane (20 mL), This mixture was warmed to room temp. Most of the hexane was removed in a vacuum, and C_6D_6 (1.5 mL) was added for preparing of NMR samples (see Figure 1). Finally after 2 d, a mixture of the stannole **7d** and the 1,4-stannabora-cyclohexa-2,5-diene **8d** was formed (see Figure 1, Figure 2, and Table 2, Table 3). ^1H NMR spectra show severe overlap of all signals, and are not assigned.

1,1-Phenyloboration of Dialkynyltin Compounds: To a stirred solution of **3a** or **3b** (1.6534 mmol) in hexane (10 mL), cooled to –78 °C, a solution of BPh_3 in toluene (0.1637 м, 10.1 mL) was added in one portion. The colorless mixture was warmed to room temp., turns yellow, and all volatile materials were removed in a vacuum to leave a red-brown oil, containing stannoles **9a** or **9b** and the 1,4-stannabora-cyclohexa-2,5-dienes **10a** or **10b**, accompanied by other unidentified side products.

$\delta\,^{119}Sn$ ($CDCl_3$) = **9a**: –23.3; **9b**: 24.1; **10a**: –152.6; **10b**: –113.7; $\delta\,^{11}B$ ($CDCl_3$) = **9a/10a**: 68.2; **9b/10b**: 67.1

The analogous phenyloboration of **3d** gave an orange-yellow oil, which contained mainly **10d**, accompanied by small amounts (<10 %) of side products, without a stannole.

10d: $\delta\,^1H$ ($CDCl_3$, [$J(^{119}Sn,^1H)$]) = 0.97 (t, 6 H, CH_3), 1.03 (t, 6 H, CH_3,), 1.29 (t, 4 H, CH_2), 1.40 (q, 4 H, CH_2), 1.45–1.81 (m, 12 H, CH_2), 2.52 [57.7] (t, 4 H, 2,5-CH_2,), 6.72–7.36 (m, 15 H, Ph).

1,1-Carboboration of Dialkynyltin Compounds with $B(C_6F_5)_3$: A solution of $B(C_6F_5)_3$ in toluene (0.01875 м, 6 mL) was kept stirring at –78 °C, and a solution of **3b** in hexane (0.1836 м, 510 µL) was added through a syringe. The mixture was stirred for 30 min at –78 °C, warmed to room temp., and stirred for further 30 min. All volatile materials were removed in a vacuum to leave a yellow solid. This material was completely soluble in C_6D_6 for NMR spectroscopic characterization. This revealed the presence of the zwitterionic intermediate **11b**, which after 16 h rearranged into the 1,4-stannabora-cyclohexa-2,5-diene **12b** [> 90 % pure (NMR)]. Further prurification (excpet of **12a** by crystallization) by chromatography on silica or Al_2O_3 was not succeesful, and, therefore, elemental analyses were not carried out.

11a, **12a**, **11c**, **12c**, and **11d**, **12d** were obtained in the same way. Suitable crystals of **11a** (m.p. >35 °C; rearrangement into **12a**) were grown from a concentrated solution in toluene at –26 °C, whereas crystals of **12a** (m.p. 110 °C, decomposition) were isolated from a saturated solution in C_6D_6 at room temp. In all cases, NMR measurements indicated quantitative reactions, and the products were yellow solids.

11a; δ ^{1}H ($CDCl_3$, $[^nJ(^{119}Sn,^1H)]$ in Hz) = 0.60–1.70 (m, 10 H), 2.50 [6.8] (s, 1 H), 6.22 [243.8] (s, 1 H, br); **12a**: δ^1H ($CDCl_3$, $[^nJ(^{119}Sn,^1H])$ = 0.81–2.05 (m, 10 H), 7.94 [93.8] (s, 2 H). **11b**: δ ^{1}H ($CDCl_3$, $[^nJ(^{119}Sn,^1H)]$) = 0.83 (t, 6 H, CH_3, 7.2 Hz), 0.98 (t, 4 H, CH_2), 1.05–1.16 (m, 4 H, CH_2), 1.22–1.32 (m, 4 H, CH_2), 2.12 [9.9] (s, 1 H), 6.30 [220.1] (s, 1 H, br); **12b**: δ ^{1}H ($CDCl_3$, $[^nJ(^{119}Sn,^1H)]$) = 0.89 (t, 6 H, CH_3), 1.01 (t, 4 H, CH_2), 1.19–1.31 (m, 4 H, CH_2), 1.41–1.52 (m, 4 H, CH_2), 7.91 [88.7] (s, 2 H); **11c**: δ ^{1}H ($CDCl_3$, $[^nJ(^{119}Sn,^1H)]$) = 2.34 [11.5] (s, 1 H), 6.26 [242.4] (s, 1 H, br), 7.22–7.28 (m, 1 H, Ph), 7.38–7.43 (m, 4 H, Ph). **12c**: δ ^{1}H ($CDCl_3$, $[^nJ(^{119}Sn,^1H)]$) = 6.85–7.60 (m, 10 H, Ph), 7.68 [88.7] (s, 2 H).

Crystal Structure Determinations of 11a and 12a: Details pertinent to the crystal structure determinations are listed in Table 4.[37] Crystals of appropriate size were selected (in perfluorinated oil at room temp.[38]), and the data collections were carried out at 133 K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinements were accomplished using SIR97,[39] SHELXL-97,[40] and WinGX.[41]

Table 4. Crystallographic data a) of the zwitterionic intermediate **11a** b) and the 1,4-stannabora-cyclohexa-2,5-diene **12a**.

	11a	**12a**
Formula	$C_{75}H_{49}B_2F_{30}Sn_2$	$C_{27}H_{12}BF_{15}Sn$
Crystal	colorless plates	colorless needles
Dimensions /mm^3	0.42 × 0.41 × 0.34	0.64 × 0.10 × 0.08
Temperature /K	133	133
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Lattice parameters		
a /pm	1146.50(7)	1096.70(6)
b /pm	1176.90(7)	2141.60(11)
c /pm	1386.30(9)	1137.30(6)
α /°	67.414(5)	90
β /°	85.488(5)	105.535(4)
γ /°	89.382(5)	90
Z	1	4
Absorption coefficient μ, /mm^{-1}	0.852	1.120
Measuring range (ϑ) /deg	1.60–25.66	1.50–25.69
Reflections collected	21493	9178
Independent reflections $[I \geq 2\sigma(I)]$	5380	3179
Absorption correction a)	no c)	numerical
Refined parameters	486	397
wR_2/R_1 $[I \geq 2\sigma(I)]$	0.0393/ 0.1034	0.0349/ 0.0750
Max./min. residual electron density /e·pm^{-3}·10^{-6}	1.297/–0.790	1.114/–0.497

a) Diffractometer: STOE IPDS II, Mo-K_α, λ = 71.073 pm, graphite monochromator. b) Crystallizes with 1.5 molecules of toluene per formula unit. c) Absorption corrections did not improve the parameter set.

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